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Solubilities of Chloride Salts of Alkali and Alkaline-Earth Metals When Sparged With Hydrogen Chloride

By E. G. Noble, D. E. Shanks, and D. J. Bauer

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
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CONTENTS

	Page
Abstract	1
Introduction	2
Materials and equipment	3
Procedure	3
Precision and accuracy	4
Results and discussion	5
Calcium chloride	5
Lithium chloride	6
Magnesium chloride	9
Potassium chloride	9
Sodium chloride	12
Summary and conclusions	13
References	14
Appendix A	15
Appendix B	16

ILLUSTRATIONS

1.	Sparging apparatus	3
2.	Solubility of $CaCl_2$ as function of HCl concentration and temperature in the $CaCl_2$-HCl-H_2O system	7
3.	Tieline plot of data for the $CaCl_2$-HCl-H_2O system at 20° C	7
4.	Tieline plot of data for the $CaCl_2$-HCl-H_2O system at 40° C	7
5.	Solubility of LiCl as function of HCl concentration and temperature in the LiCl-HCl-H_2O system	8
6.	Tieline plot of the data for the LiCl-HCl-H_2O system at 20° C	8
7.	Tieline plot of the data for the LiCl-HCl-H_2O system at 40° C	8
8.	Solubility of $MgCl_2$ as function of HCl concentration and temperature in the $MgCl_2$-HCl-H_2O system	10
9.	Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 20° C	10
10.	Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 40° C	10
11.	Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 60° C	11
12.	Solubility of KCl as function of HCl concentration and temperature in the KCl-HCl-H_2O system	11
13.	Solubility of NaCl as function of HCl concentration and temperature in the NaCl-HCl-H_2O system	12

TABLES

B-1.	$CaCl_2$-HCl-H_2O system	16
B-2.	LiCl-HCl-H_2O system	16
B-3.	$MgCl_2$-HCl-H_2O system	16
B-4.	KCl-HCl-H_2O system (solution)	17
B-5.	NaCl-HCl-H_2O system (solution)	17

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	L/min	liter per minute
°C	degree Celsius	m	meter
cm^3/min	cubic centimeter per minute	mL	milliliter
		mL/min	milliliter per minute
g	gram		
h	hour	mm	millimeter
		pct	weight percent
hp	horsepower		
in	inch	psig	pound (force) per square inch, gauge
L	liter	rpm	revolution per minute
lb	pound	W	watt

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SOLUBILITIES OF CHLORIDE SALTS OF ALKALI AND ALKALINE-EARTH METALS WHEN SPARGED WITH HYDROGEN CHLORIDE

By E. G. Noble,[1] D. E. Shanks,[2] and D. J. Bauer[3]

ABSTRACT

The effects of hydrogen chloride (HCl) concentration and temperature on the solubility and hydration state of the alkali chlorides LiCl, NaCl, and KCl and the alkaline-earth chlorides, $MgCl_2$, and $CaCl_2$ were investigated by the Bureau of Mines. Saturated aqueous solutions of the chlorides were sparged with HCl gas at temperatures of 20°, 40°, and 60° C. Increased HCl concentration caused decreased salt solubility because of the common ion effect. Aqueous solubilities for the chlorides of Ca, Li, Mg, K, and Na ranged from 42.6, 45.2, 35.2, 25.5, and 26.1 pct, respectively, at 20° C to 56.9, 49.4, 37.6, 31.0, and 27.0 pct, respectively, at 60° C. In solutions sparged to HCl saturation, solubilities for these chlorides ranged from 22.4, 26.5, 3.0, 1.3, and 0.05 pct, respectively, at 20° C to 53.2, 48.8, 28.3, 2.6, and 0.8 pct, respectively, at 60° C. The solubilities of LiCl and $CaCl_2$ in HCl solution were high because HCl solubility is low in these solutions. The chloride salts of Ca, Li, and Mg formed hydrates, which depended on temperature and HCl concentration. Monohydrates for LiCl, tetrahydrates and hexahydrates for $MgCl_2$, and dihydrates, tetrahydrates, and hexahydrates for $CaCl_2$ were obtained.

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INTRODUCTION

Separations and purifications can be enhanced in chloride hydrometallurgical systems by sparging crystallization with hydrogen chloride gas. For example, in the Bureau's hydrochloric acid process for producing alumina from clay, crystalline aluminum chloride hexahydrate of sufficient purity to meet aluminum industry standards is recovered from impure pregnant liquor by the decrease in solubility caused by hydrogen chloride gas addition. Implementation of sparging crystallization technology is hampered by a lack of solubility and kinetic data on metal chloride-hydrogen chloride-water systems.

The Bureau of Mines is especially interested in promoting research in the metallurgy of elements of strategic and critical economic importance. A recent paper by Shanks and Noble (1)[4] presented the results of solubility and crystal composition studies of the chlorides of cobalt, manganese, and nickel. In this study and the clay-HCl process for producing alumina, there was insufficient information on the solubility and crystal characteristics of associated elements that must be separated from the elements of interest in the leach-purification scheme. Five such elements of concern are lithium, sodium, potassium, magnesium, and calcium.

The goals of this research were to expand the data base for sparging crystallization of chlorides of the alkali and alkaline-earth elements, to determine the solubility of HCl and the chlorides in aqueous solutions, and to confirm that sparging crystallization produced the same results as equilibrium data in the literature.

Considerable data are available on the aqueous solubilities of the alkali and alkaline-earth chlorides, and some data are available on the solubilities in metal chloride-HCl-H_2O systems. However, these data were gathered in long-term equilibrium tests using closed containers and predetermined amounts of constituents. Publications prior to 1956-57 are summarized in Linke-Seidell (2). In more recent publications, Potter and Clynne reported the aqueous solubilities for NaCl, KCl, and $CaCl_2$ (3) and the solubilities of NaCl and KCl in aqueous HCl (4). The $MgCl_2$-HCl-H_2O system was studied by Dühne (5) at temperatures of -55° to 80° C and by Berecz and Bader (6) at 15° to 50° C. These data show that the alkali and alkaline-earth chlorides decrease in solubility with increasing HCl concentration, but only limited data were collected at 20° to 60° C and no kinetic data are available. In this study, the metal chloride-hydrogen chloride-water systems were studied at 20°, 40°, and 60° C. These temperatures uniformly cover the expected operating range of metal chloride separations. At temperatures above 60° C, a pressure system would be necessary for the metal chloride solutions to absorb sufficient HCl.

In metallurgical applications, kinetic and crystal characteristic data are important. Kinetic information is needed to determine how rapidly equilibrium is achieved. Crystallization schemes involve sparging with HCl gas, and the final crystal form is important for solid-liquid separation and purification. Reports by Shanks and Noble (1) and Shanks, Kisele, and Bauer (7) showed that equilibrium is rapidly achieved in the $CoCl_2$-HCl-H_2O, $MnCl_2$-HCl-H_2O, $NiCl_2$-HCl-H_2O, and $AlCl_3$-HCl-H_2O systems, and that sparging and equilibrium studies gave comparable results (8-10), thus allowing existing solubility data to be used to predict sparging results and vice versa. Unfortunately, this is not universally true. Ongoing research by the Bureau of Mines shows that some systems, such as $CrCl_3$-HCl-H_2O and $FeCl_3$-HCl-H_2O, do not equilibrate rapidly and must be studied with time as an added parameter.

[4]Underlined numbers in parentheses refer to the items in the list of references preceding the appendixes.

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MATERIALS AND EQUIPMENT

Sparging was performed in a 3-L water-jacketed borosilicate glass resin reaction kettle with a four-port lid (fig. 1). Temperature was monitored with a mercury thermometer marked in 0.1° C increments. The circulator bath, pressure regulators, flowmeters, and stirring apparatus were described previously (1).

Each experiment started with a saturated solution of the metal chloride (reagent grade). Reagents used to make saturated solutions included $CaCl_2 \cdot 2H_2O$, LiCl, $MgCl_2 \cdot 6H_2O$, KCl, and NaCl. The sparging gas was technical-grade hydrogen chloride, >99 pct HCl (impurities: hydrocarbons, water, carbon dioxide, and inert materials). Reagents used for analytical purposes were 0.1000N HCl [standardized at 25° C against 2-amino-2(hydroxymethyl)-1,3-propanediol (TRIS)], 0.1000N carbonate-free NaOH, and silver nitrate, $AgNO_3$, ACS reagent grade.

Crystal-free samples of solution were removed from the crystallizer through a coarse-porosity, fritted-glass gas-dispersion tube, 250 mm long, with an 8-mm-diam stem and a 12-mm-diam cylindrical disk. Volumetric flasks used for analysis of chloride salt samples were 100-mL capacity ±0.08 mL at 20° C. Hydrogen and total chloride ion concentrations were determined using an automatic titrating apparatus with a motor-driven burette, utilizing a standard pH electrode for hydrogen ion titrations and a chloride ion-specific electrode for chloride titrations. Reference electrodes were sleeve, double-junction, calomel-internal, with salt bridge filling solution of sodium acetate-sodium nitrate.

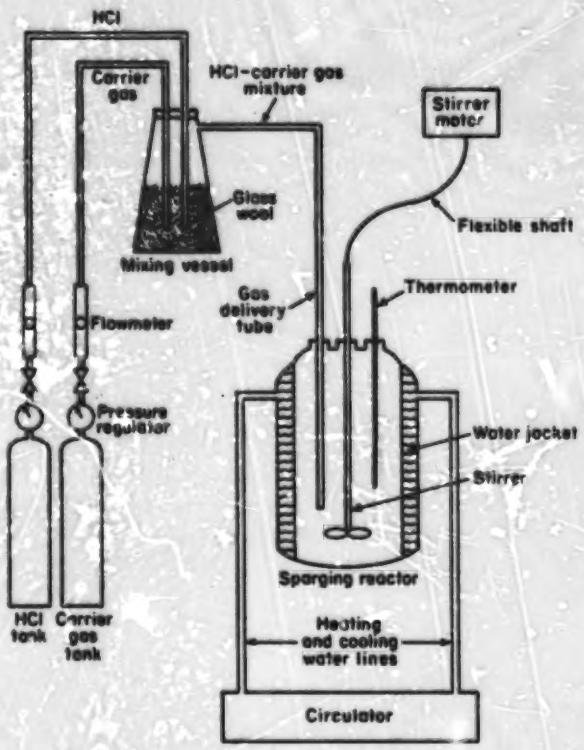

FIGURE 1. - Sparging apparatus.

PROCEDURE

Saturated chloride solutions were prepared by heating 1 to 2 L of water to slightly greater than the desired temperature, slowly stirring in the chloride until excess solids remained for at least 24 h after the last addition, and cooling to the desired temperature. The solutions were maintained at temperatures of 20°, 40°, or 60° C and sparged with a mixture of HCl and carrier gases until saturated with HCl. The HCl passing through the flowmeter was regulated at 10 psig and adjusted to a flow rate of 850 mL/min. The carrier gas, air or nitrogen, was regulated at 10 psig and delivered at a flow rate of 200 mL/min through the flowmeter. Previous work (7) had shown that the use of a carrier gas resulted in larger, purer crystals and fewer problems with sparger tip plugging. The stirrer speed was adjusted to the minimum speed that would keep the solids in suspension. The HCl flow rate of 850 mL/min was the fastest flow that could be utilized without exceeding the cooling capacity of the circulator (HCl absorption is exothermic) and gave a reasonable sampling frequency. The chloride salt solution was sampled prior to sparging, and hourly until the conclusion of the

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experiment. Approximately 5-mL samples were drawn from the slurry through a fritted-glass gas-dispersion tube to insure that no solids were removed. The solution was added to a volumetric flask (100±0.08 mL at 20° C) approximately half full of a weighed amount of water. The volumetric flask was weighed after the sample was added and again after the flask was filled to the 100 mL mark. This procedure minimized loss of HCl and allowed for calculation of the weight of the sample and the density of the diluted sample. The specific gravity was determined directly on solutions separated from 20° C slurries with a Mettler-Paar[5] DMA 35 density meter, ±0.001 accuracy. Since this instrument can only be used in the 10° to 30° C range, the specific gravity of the 40° and 60° C solutions was determined by weighing a 5-mL sample of the solution. To obtain residue samples, approximately 5 mL of slurry was collected with a ladle. The solids were partially dried by blotting on glass-fiber filter paper, added to tared volumetric flasks half full of water, and handled in the same manner as the liquid samples.

One-milliliter aliquots were withdrawn from the volumetric flasks, weighed, and the weight was divided by the density of the solution. The HCl concentration was determined by diluting a 1-mL aliquot to 50 mL with water and titrating with standardized 0.1000N NaOH. The automatic titrator determined the end point as the inflection point of the titration curve and printed out the volume of titrant consumed in reaching the end point. Hydrogen chloride concentration was calculated from equation A-1 in Appendix A.

Metal chloride concentration was determined by titrating a 1-mL aliquot with standardized 0.100N silver nitrate ($AgNO_3$) and detecting the change in chloride concentration with a chloride specific ion electrode. The end-point volume was converted to metal chloride concentration by equation A-2.

Metal chloride concentration was checked by a gravimetric technique in which 25-mL aliquots were dried under heat lamps, heated to 200° C in a muffle furnace, cooled in a vacuum desiccator, and weighed as the anhydrous chloride. Atomic absorption spectroscopy on low metal chloride concentrations was used to supplement the gravimetric results.

The experiments were terminated when HCl sparging ceased to influence the HCl and chloride salt concentrations. The wet residue and solution compositions were plotted on triangular coordinate paper, and tielines were constructed to determine crystal composition by Schreinemakers' wet residue method (11).

PRECISION AND ACCURACY

A potential accuracy problem was chemical nonequilibrium of the analyzed solutions. In conventional equilibrium studies, premeasured quantities of reagents are shaken in closed containers for extended periods at constant temperature. Periodic readings determine when the systems are in equilibrium. With the sparging technique, concentrations of reagents are constantly changing, and HCl can be lost from solution unless equilibrium is rapid. However, measurements made after sparged slurries were allowed to stand overnight remained unchanged from those taken at the cessation of sparging, showing that the reaction kinetics are fast and HCl is not easily lost from solution. Metal chloride and HCl concentrations changed by less than 0.1 pct. Bottle tests of 2-week duration gave results almost identical to those of sparging, and both compared favorably with equilibrium data from previous work.

The $AgNO_3$ titration of chloride content represented the precision-limiting step in the solubility determinations. Several hundred titrations of 0.1000N HCl with $AgNO_3$ and NaOH were made during this research to determine chloride and HCl concentrations. Average values of the titrant concentrations were 0.0991 ±0.0010N for the $AgNO_3$ and

[5]Reference to specific manufacturers or brand names does not imply endorsement by the Bureau of Mines.

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0.1000 ±0.0002N for the NaOH. This represents a variation of ±0.05 mL for the $AgNO_3$ and ±0.025 mL for the NaOH, and an accuracy of 2 to 0.7 pct for chloride and 10 to 0.4 pct for hydrogen concentrations. Since the contribution of chloride from the HCl must be subtracted from the total chloride concentration, the two errors are additive.

Some of the ancillary measurements had larger relative errors but had no bearing on the precision or accuracy of the solubility work. Previous work had shown that the HCl flow rate was not an important parameter at flow rates less than 1,300 mL/min (7). The 850-mL/min flow rate had an estimated precision of ±5 pct. Specific gravity measurements at 40° and 60° C showed considerable scatter and varied as much as ±3 pct; therefore, the values reported for specific gravity in tables B-1 to B-5, appendix B, were determined from smoothed curves.

Other sources of error were minor. Pipetting errors were eliminated by weighing the aliquot and the total sample and dividing the weight of the aliquot by the weight of one one-hundredth of the total sample to obtain correspondingly accurate volumes. The volumetric flasks were certified to contain 100 mL ±0.08 mL of solution, a maximum error of 0.08 pct. The balance used for weighing the flasks has an accuracy of 0.01 g ±0.006 g. Temperatures were measured with thermometers marked in 0.1° C increments and estimatable to 0.02° C. Observed temperature variations were within 0.05° C. Each thermometer was calibrated against a set of National Bureau of Standards (NBS) certified thermometers and read within ±0.1° C of the certified temperature in the 20° to 60° C range. Temperature variations of 0.1° C would lead to a maximum metal chloride concentration error of 0.1 pct.

RESULTS AND DISCUSSION

The five systems varied in their response to increased temperature and hydrogen chloride concentration. Although all chlorides showed increased aqueous solubility with increased temperature, the increase was greatest for $CaCl_2$, 42.6 to 56.9 pct, and least for sodium chloride, 26.1 to 27.0 pct. HCl absorption was lowest in the lithium chloride system and highest in the potassium and sodium chloride systems. There are few solubility data in the literature for these metal chloride-hydrogen chloride-water systems at 20°, 40°, and 60° C to compare with the data from this study. However, the solubilities of the potassium and sodium chloride systems do not vary significantly with increased temperature. The 20° C data compare closely with the literature data for these systems at 25° C (2). The results confirmed that rapid equilibrium was attained in these systems with HCl-sparging crystallization.

Data for the five systems at the temperature ranges investigated are summarized in tables B-1 to B-5. The information in each table represents a composite of analyses from the several analytical procedures used and will be discussed in the following section. From these tabulations, the solubility curves in figures 2, 5, 8, 12, and 13 and the tieline diagrams in figures 3, 4, 6, 7, and 9-11 were plotted. Since potassium and sodium chlorides do not form hydrates, the wet residues from the systems containing these salts were not analyzed.

CALCIUM CHLORIDE

The published aqueous solubility data on calcium chloride shows discrepancies. Potter and Clynne (3) state that the data reported in Linke-Seidell (2) are too high, especially at temperatures above 28° C. Additionally, Linke-Seidell reported several different values for each temperature increment between 30° and 45° C. Potter and Clynne propose that these differences are due to the high viscosity of the $CaCl_2$ solutions, which allows small crystals to remain suspended almost indefinitely and causes density stratification. Their method for determining solubilities did not depend on obtaining representative samples of the fluid for analysis. The samples analyzed in this research were obtained by drawing

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a representative sample of the reaction solution through a fritted glass tube. The technique prevents the inclusion of suspended solids in the sampled solution. To prevent density stratification of the reaction solution, it was necessary to stir the samples vigorously. The data obtained showed solubilities between those reported by Linke-Seidell and Potter and Clynne. Extrapolation of the data for 20°, 40°, and 60° C from the solubility curves of Potter and Clynne was required for the comparison.

Unlike most hydrated chloride salts, commercial calcium chloride is not in its most hydrated form. The $CaCl_2$ crystals in a saturated aqueous solution are more hydrated than the reagent. Linke-Seidell and Potter and Clynne agree on the transition temperatures for the change of hydration states:

$$CaCl_2 \cdot 6H_2O \rightleftharpoons CaCl_2 \cdot 4H_2O \qquad (1)$$

at 30.1° C, and

$$CaCl_2 \cdot 4H_2O \rightleftharpoons CaCl_2 \cdot 2H_2O \qquad (2)$$

at 45.1° C. Tieline data and visual observation confirmed that $CaCl_2$ crystals precipitated from saturated aqueous solution in the hexahydrate form at 20° C, the tetrahydrate at 40° C, and the dihydrate at 60° C.

Calcium chloride concentration as a function of HCl concentration at 20° C is tabulated in table B-1 and plotted in figures 2 and 3. The initial slope of the solubility curve (fig. 2) was -1.0 pct $CaCl_2$/pct HCl. The aqueous solubility was 42.6 pct $CaCl_2$ (Linke-Seidell, 42.7 pct, Potter and Clynne, 42.1 pct). Minimum $CaCl_2$ solubility of 22.4 pct occurred at HCl saturation, 25.7 pct. The transition from the hexahydrate to the tetrahydrate was at 34 pct $CaCl_2$ and 12 pct HCl. Tieline data in figure 3 show a change in hydrates between 12 and 18 pct HCl concentration. The transition point was confirmed by the change from an exothermic to an endothermic reaction. When the transition was made, the absorption reaction was again exothermic.

Calcium chloride concentration as a function of HCl concentration at 40° C is tabulated in table 1 and plotted in figures 2 and 4. Calcium chloride solubility in water was 55.0 pct. Linke-Seidell report 53.4, 55.9, and 56.2 pct and Potter and Clynne's data indicate 53.3 pct. Minimum solubility was 44.6 pct at HCl saturation of 9.2 pct. The initial slope of the solubility curve in figure 2 was -1.0 pct $CaCl_2$/pct HCl. The transition from $CaCl_2 \cdot 4H_2O$ to $CaCl_2 \cdot 2H_2O$ was marked by a small inflection point at 47.2 pct $CaCl_2$, 7.2 pct HCl. Between 6.8 and 7.2 pct HCl, the sparging crystallization was endothermic. At higher HCl concentrations, the crystallization reaction was exothermic. Tieline data show that the hydrate change occurs between 47.4 pct $CaCl_2$, 7.0 pct HCl, and 45.4 pct $CaCl_2$, 8.5 pct HCl.

Calcium chloride concentration as a function of HCl concentration at 60° C is tabulated in table B-1 and plotted in figure 2. The residue samples were not analyzed because visual observation indicated that the crystals did not change from the dihydrate form on dissolution in water and they were unchanged at maximum HCl absorption of 3.6 pct. The solubility in water was 56.9 pct $CaCl_2$ (Linke-Seidell, 57.8 pct, Potter and Clynne, 56.7 pct). Minimum calcium chloride solubility was 53.2 pct at 3.6 pct HCl. The slope of the solubility curve was -1.0 pct $CaCl_2$/pct HCl.

LITHIUM CHLORIDE

Lithium chloride concentration as a function of HCl concentration at 20° C is tabulated in table B-2 and plotted in figures 5 and 6. The LiCl solubility curve in figure 5 is linear with a slope of -1.0 pct LiCl/pct HCl. Aqueous LiCl solubility was 45.2 pct. Minimum solubility of 26.5 pct LiCl was obtained at 18.6 pct HCl. The viscous solution at this composition would absorb no more HCl. There is no inflection point in the curve of the solubility data, and no phase change is indicated in the tieline plot; therefore, only a single hydrate form exists at 20° C. This research did not indicate whether the hydrate is the monohydrate or dihydrate because the tielines did not intersect at either of

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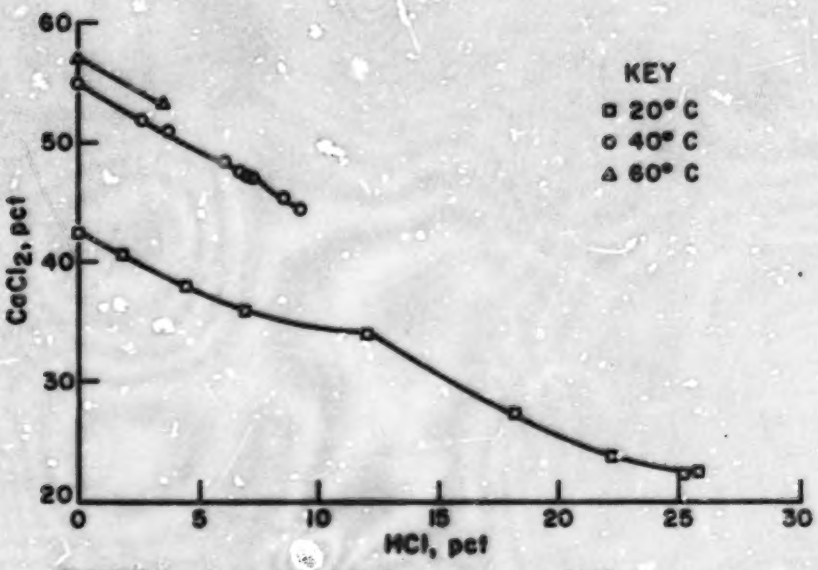

FIGURE 2. - Solubility of $CaCl_2$ as function of HCl concentration and temperature in the $CaCl_2$-HCl-H_2O system.

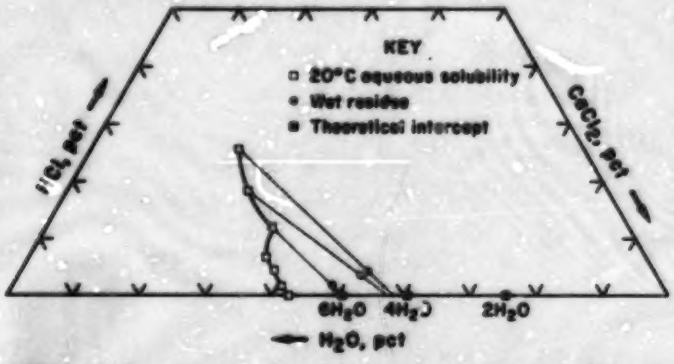

FIGURE 3. - Tieline plot of the data for the $CaCl_2$-HCl-H_2O system at 20° C.

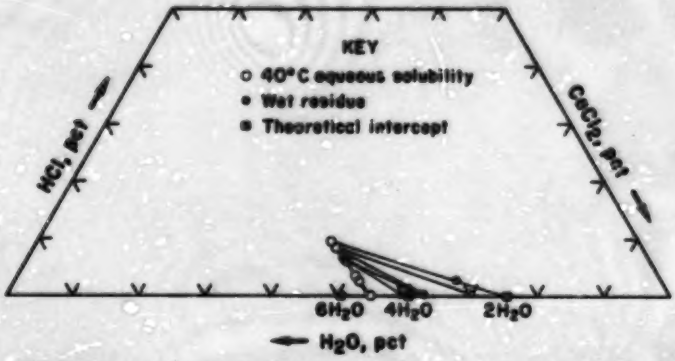

FIGURE 4. - Tieline plot of the data for the $CaCl_2$-HCl-H_2O system at 40° C.

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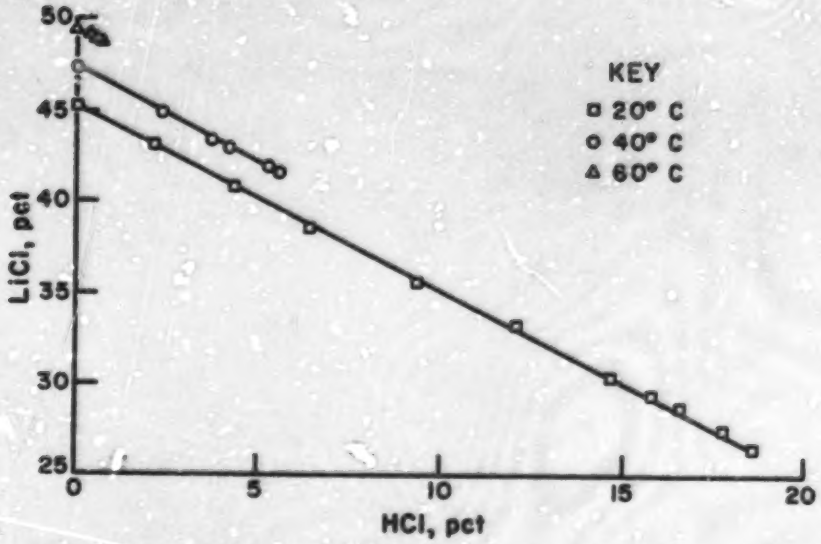

FIGURE 5. - Solubility of LiCl as function of HCl concentration and temperature in the LiCl-HCl-H_2O system.

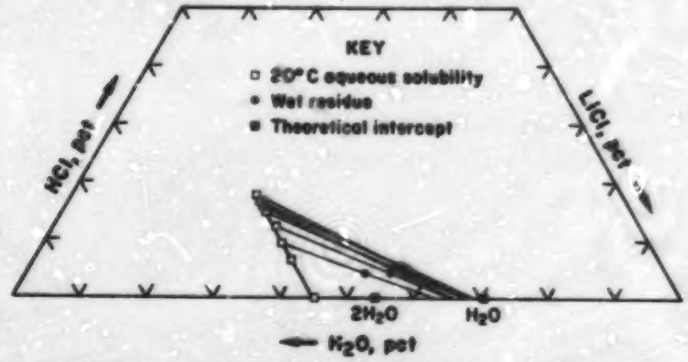

FIGURE 6. - Tieline plot of the data for the LiCl-HCl-H_2O system at 20° C.

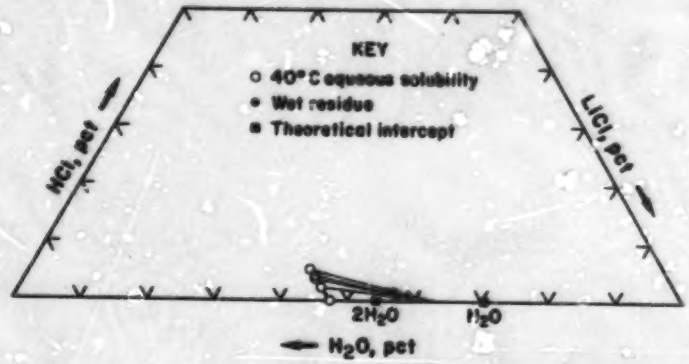

FIGURE 7. - Tieline plot of the data for the LiCl-HCl-H_2O system at 40° C.

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those compositions. The monohydrate is assumed because the composition of the residue is more anhydrous than is the theoretical composition of $LiCl \cdot 2H_2O$. The scatter in the tieline data reflected the problems experienced in preparing the residue samples. The viscous nature of the solution prevented adequate removal from the residue, and the low HCl concentration in the samples magnified the analytical errors. The Linke-Seidell data do not show the composition of the solid phase at 20° C. References listed in Linke-Seidell show phase changes in the range of 18.5° to 19.1° C for the dihydrate to monohydrate change and a range of 93° to 100° C for the monohydrate to anhydrous change.

Lithium chloride concentration as a function of HCl concentration at 40° C is tabulated in table B-2 and plotted in figures 5 and 7. The LiCl solubility curve for 40° C has the same slope as the 20° C curve. The solubility of LiCl in water was 47.3 pct, the same value reported in Linke-Seidell. Lithium chloride solubility decreased to 41.6 pct at maximum HCl solubility of 5.5 pct. The tieline data show that the solid phase was $LiCl \cdot H_2O$. There is no inflection point in the solubility curve to indicate a phase change.

Lithium chloride concentration as a function of HCl concentration at 60° C is tabulated in table B-2 and plotted in figure 6. Aqueous LiCl solubility was 49.4 pct; Linke-Seidell reported 49.6 pct. Extensive sparging resulted in an HCl solubility maximum of 0.7 pct at a lithium chloride solubility minimum of 48.8 pct. Only one residue sample was analyzed and its low HCl concentration gave an imprecise tieline. The resulting tieline indicated that lithium chloride was present as the monohydrate in the $LiCl-HCl-H_2O$ system at 60° C. Yodis used the ability of lithium chloride to break the hydrogen chloride azeotropes in developing a process for producing anhydrous hydrogen chloride (12).

MAGNESIUM CHLORIDE

Magnesium chloride concentration as a function of HCl concentration at 20° C is tabulated in table B-3 and plotted in figures 8 and 9. Magnesium chloride solubility in water was 35.2 pct. (Linke-Seidell reported 35.3 pct.) Sparging with HCl decreased the solubility of $MgCl_2$ to 3.0 pct at HCl saturation of 36.3 pct. The $MgCl_2$ solubility curve in figure 8 is linear with a slope of -1.0 pct $MgCl_2$/pct HCl up to a HCl concentration of 16.6 pct. A small inflection point occurs at 25.5 pct HCl and 11.9 pct $MgCl_2$ and corresponds to the transition from $MgCl_2 \cdot 6H_2O$ to $MgCl_2 \cdot 4H_2O$ in the salted-out crystals. Tieline data in figure 9 show the breakpoint at the same place.

Table B-3 contains the tabulated data of magnesium chloride concentration as a function of HCl concentration at 40° C. The data are plotted in figures 8 and 10. The magnesium chloride solubility in water was 36.0 pct compared with 36.5 pct in Linke-Seidell. Minimum solubility was 15.3 pct at HCl saturation of 23.6 pct. The solubility curve in figure 8 was almost linear, and the initial slope was -0.9 pct $MgCl_2$/pct HCl. The solubility curve did not indicate a change in the crystal state during HCl sparging, and the tieline data in figure 10 confirm that all crystals were in the hexahydrate form.

Magnesium chloride concentration as a function of HCl concentration at 60° C is tabulated in table B-3 and plotted in figures 8 and 11. The $MgCl_2$ solubility curve in figure 8 was linear with a slope of -0.9 pct $MgCl_2$/pct HCl. Magnesium chloride solubility ranged from 37.6 pct in water to 28.3 pct at HCl saturation of 10.4 pct. Linke-Seidell reported $MgCl_2$ solubility in water at 60° C as 37.9 pct and Dähne (5) reported 37.7 pct. The solubility curve from Dähne's data matched the curve from the solubility data from this study. Tieline data in figure 11 show that crystals salted out at 60° C with HCl sparging are in the hexahydrate form.

POTASSIUM CHLORIDE

Potassium chloride concentration as a function of HCl concentration at 20° C is tabulated in table B-4 and plotted in figure 12. The initial slope of the solubility curve is -1.6 pct KCl/pct HCl.

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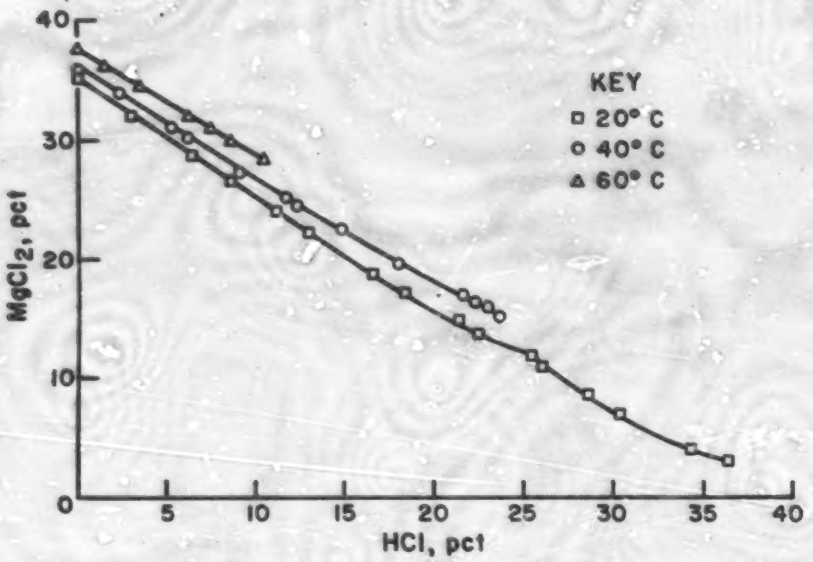

FIGURE 8. - Solubility of $MgCl_2$ as function of HCl concentration and temperature in the $MgCl_2$-HCl-H_2O system.

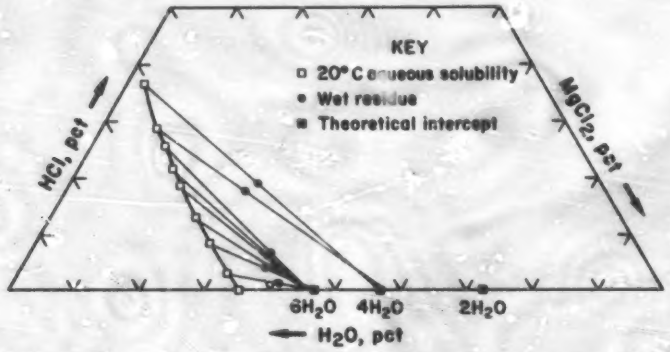

FIGURE 9. - Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 20° C.

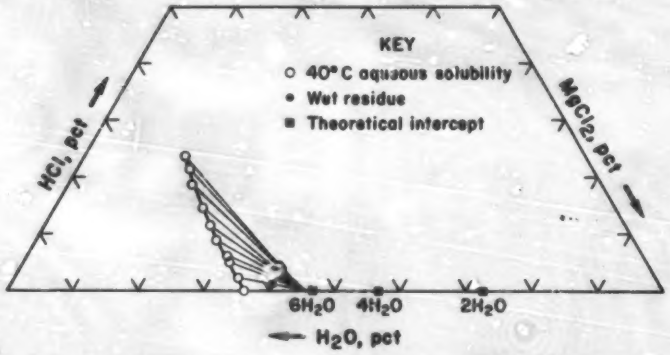

FIGURE 10. - Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 40° C.

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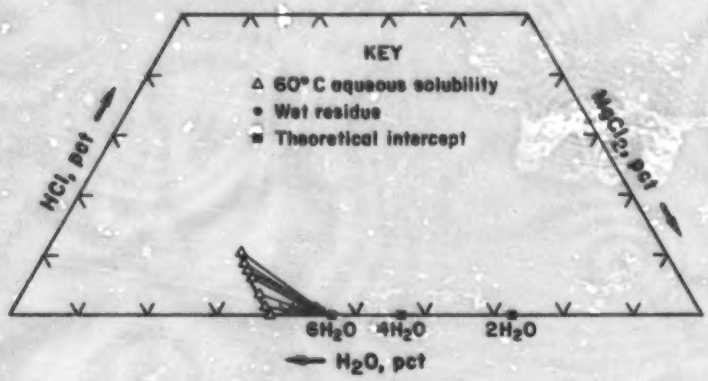

FIGURE 11. - Tieline plot of the data for the $MgCl_2$-HCl-H_2O system at 60° C.

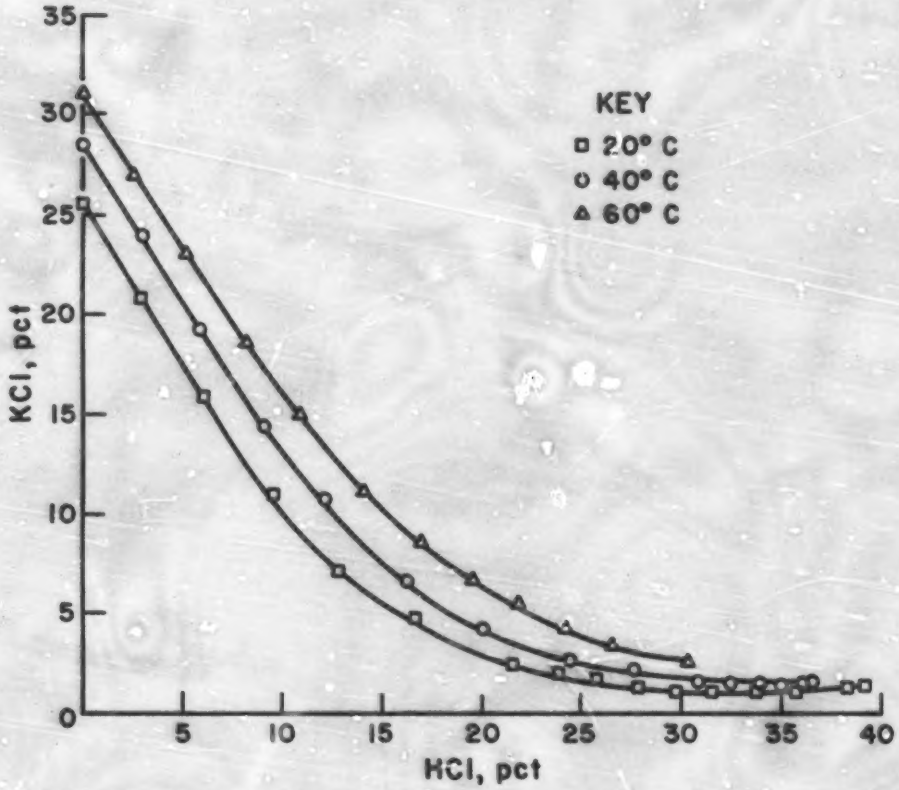

FIGURE 12. - Solubility of KCl as function of HCl concentration and temperature in the KCl-HCl-H_2O system.

The solubility of the KCl in water was 25.5 pct (Linke-Seidell also reported 25.5 pct) and obtained a minimum of 1.1 pct at 29.7 pct HCl. The KCl solubility increased slightly to 1.3 pct at HCl saturation of 39.1 pct. Linke-Seidell reported data for the system KCl-HCl-H_2O at 25° C; the curve plotted from the data is parallel to the 20° C curve and shows a slight increase in KCl solubility at HCl saturation.

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Potassium chloride concentration as a function of HCl concentration at 40° C is tabulated in table B-4 and plotted in figure 12. The solubility curve is similar to the 20° C curve, and the initial slope is -1.5 pct KCl/pct HCl. Aqueous solubility was 28.4 pct KCl (compared to 28.6 pct in Linke-Seidell). Minimum KCl solubility of 1.5 pct was at 35.0 pct HCl. There was a slight increase in solubility to 1.7 pct at HCl saturation of 36.5 pct.

Potassium chloride concentration as a function of HCl concentration at 60° C is tabulated in table B-4 and plotted in figure 12. The slope of the curve is -1.5 pct KCl/pct HCl and is approximately parallel to the 20° and 40° C curves. Potassium chloride solubility ranged from 31.0 pct in water to 2.6 pct at HCl saturation of 30.4 pct. Linke-Seidell reported aqueous solubility at 60° C as 31.4 pct.

SODIUM CHLORIDE

Sodium chloride concentration as a function of HCl concentration at 20° C is tabulated in table B-5 and plotted in figure 13. The aqueous solubility data for NaCl reported in Linke-Seidell ranges from 26.3 pct to 28.2 pct between 0° and 100° C. The solubility curves for the NaCl-HCl-H_2O system at 20°, 40°, and 60° C are parallel and show little difference in solubility. When the temperature of the system increased, HCl concentration at saturation was lowered. At 20° C, the initial slope of the solubility curve was -1.4 pct NaCl/pct HCl. The NaCl solubility ranged from 26.1 pct in water to 0.05 pct at 39.1 pct HCl. Linke-Seidell reported NaCl solubility in water as 26.4 pct.

Sodium chloride concentration as a function of HCl concentration at 40° C is tabulated in table B-5 and plotted in figure 13. The initial slope of the solubility curve was -1.4 pct NaCl/pct HCl. Linke-Seidell reported aqueous solubility at 40° C as 26.7 pct. The aqueous solubility was 26.6 pct and the solubility at 37.0 pct HCl was 0.1 pct.

Sodium chloride concentration as a function of HCl concentration at 60° C

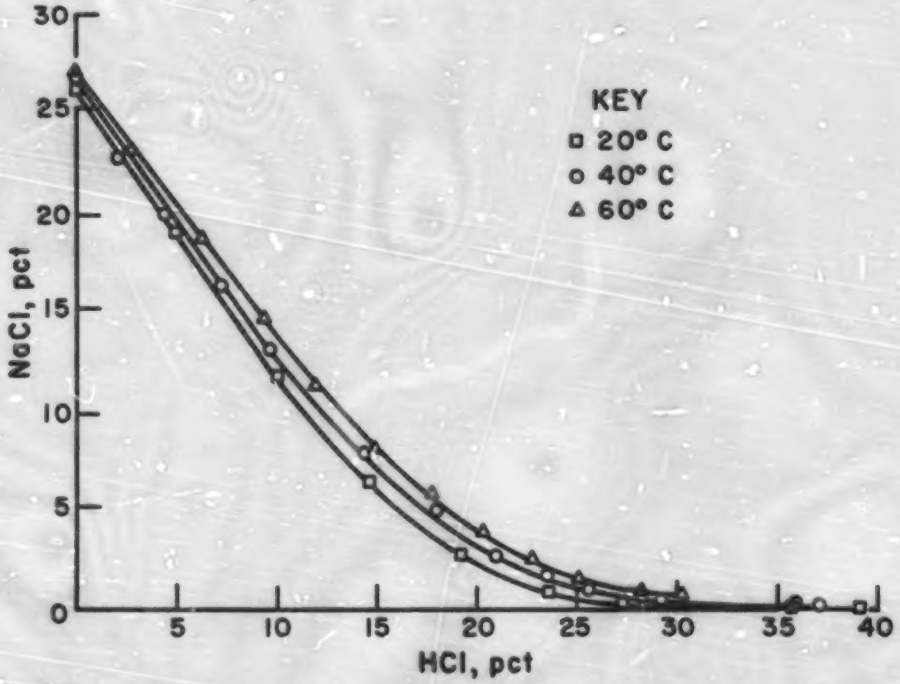

FIGURE 13. - Solubility of NaCl as function of HCl concentration and temperature in the NaCl-HCl-H_2O system.

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is tabulated in table B-5 and plotted in figure 13. The solubility curve had an initial slope of -1.3 pct NaCl/pct HCl. The NaCl solubility ranged from 27.0 pct in water (Linke-Seidell, 27.0 pct) to 0.5 pct at HCl saturation of 30.2 pct.

SUMMARY AND CONCLUSIONS

Solubility data from hydrogen chloride sparging of saturated solutions of alkali and alkaline-earth chlorides agreed with literature values obtained by conventional equilibrium testing. For the systems and conditions reported, the solubility data from the sparging crystallization method are as valid as the data from the slower bottle-test equilibrium methods. Conventional equilibrium data can be used to predict the effects of HCl sparging on these aqueous chloride salts.

The chlorides of Ca, Li, Mg, K, and Na decreased in solubility and crystallized out of solution when sparged with HCl gas because of the common ion effect. The crystallization was almost total for sodium and potassium chlorides. Lithium chloride was least susceptible to salting out because much less HCl was absorbed. Calcium chloride was similar to lithium chloride in behavior, and magnesium chloride was similar to sodium and potassium chlorides. The effect of temperature on hydrogen chloride solubility was greatest for lithium chloride and least for sodium chloride. In saturated HCl, the saturation composition of $CaCl_2$, LiCl, $MgCl_2$, KCl, and NaCl were, as follows, in percent:

	20° C	40° C	60° C
$CaCl_2$..	22.4	44.6	53.2
LiCl...	26.5	41.6	48.8
$MgCl_2$..	3.0	15.3	28.3
KCl....	1.3	1.7	2.6
NaCl...	.05	.1	.8

The salted-out chlorides of Na and K were anhydrous. Lithium chloride formed monohydrate crystals. Magnesium chloride formed the hexahydrate in saturated aqueous solutions at 20°, 40°, and 60° C. At HCl concentrations above 26.0 pct at 20° C, the tetrahydrate was present. Calcium chloride formed the hexahydrate in saturated aqueous solutions at 20° C and low concentrations of hydrochloric acid. The tetrahydrate was formed between HCl between concentrations of 12 and 18 pct. Increasing the temperature or the hydrochloric acid concentration caused transformation to lower hydrates. At 40° C calcium chloride formed the tetrahydrate at HCl concentrations up to 7.2 pct and formed the dihydrate at higher concentrations. Only the dihydrate existed at 60° C.

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APPENDIX A

A-1. - Equation for calculating hydrogen chloride concentration

$$R_1 = E_1 \times C_1 \times C_2 / C_3 \times C_4,$$

where R_1 = concentration of HCl, pct,

E_1 = NaOH volume, mL,

C_1 = 364.6 = meq-wt HCl × volumetric flask volume × conversion factor wt-fraction to wt-pct,

C_2 = 0.1000 = NaOH concentration, N,

C_3 = volume of aliquot crated, mL,

and C_4 = weight of sample taken from crystallizer, g.

A-2. - Equation for calculating metal chloride concentration

$$R_2 = [(E_2 \times C_6 / C_7) - R_3](C_5 / C_4),$$

where R_2 = metal chloride concentration, pct,

E_2 = $AgNO_3$ volume, mL,

C_5 = meq-wt metal chloride × volumetric flask volume × conversion factor wt-fraction to wt-pct. (554.93 for $CaCl_2$, 423.92 for LiCl, 476.09 for $MgCl_2$, 745.55 for KCl, and 584.43 for NaCl),

C_6 = $AgNO_3$ concentration, N,

C_7 = volume of aliquot titrated with $AgNO_3$, mL,

and R_3 = correction for chloride contributed by HCl = $E_1 \times C_2 / C_3$.

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APPENDIX B

TABLE B-1. - $CaCl_2$-HCl-H_2O system

Solution			Wet residue	
HCl, pct	$CaCl_2$, pct	sp gr	HCl, pct	$CaCl_2$, pct
20° C				
0.0	42.6	1.42	NA	NA
1.9	40.8	1.41	NA	NA
4.5	38.1	1.40	NA	NA
6.9	36.0	1.39	NA	NA
12.0	34.1	1.39	2.0	48.1
18.2	27.5	1.35	3.4	51.9
22.2	23.9	1.33	NA	NA
25.1	22.3	1.33	NA	NA
25.7	22.4	1.33	4.3	52.1
40° C				
0.0	55.0	1.52	NA	NA
2.7	52.0	1.51	NA	NA
3.8	51.0	1.50	NA	NA
6.1	48.5	1.49	0.5	62.2
6.8	47.7	1.48	.2	59.1
7.0	47.4	1.48	.4	62.8
7.2	47.2	1.48	NA	NA
8.5	45.4	1.47	.5	69.4
9.2	44.6	1.46	2.9	66.3
60° C				
0.0	56.9	1.57	NA	NA
3.6	53.2	1.55	NA	NA

NA Not analyzed.

TABLE B-2. - LiCl-HCl-H_2O system

Solution			Wet residue	
HCl, pct	LiCl, pct	sp gr	HCl, pct	LiCl, pct
20° C				
0.0	45.2	1.29	NA	NA
2.1	43.1	1.28	NA	NA
4.3	40.8	1.28	NA	NA
6.4	38.6	1.28	NA	NA
9.4	35.6	1.28	4.4	50.5
12.1	33.2	1.27	4.2	54.4
14.7	30.4	1.27	5.0	54.4
15.8	29.4	1.26	3.7	57.8
16.6	28.7	1.26	5.4	56.4
17.8	27.5	1.26	4.9	56.6
18.6	26.5	1.26	NA	NA
40° C				
0.0	47.3	1.32	NA	NA
2.3	44.9	1.32	0.9	57.0
3.7	43.4	1.31	1.5	55.1
4.2	43.0	1.31	1.6	55.5
5.2	41.8	1.30	1.7	55.9
5.5	41.6	1.30	NA	NA
60° C				
0.0	49.4	1.32	NA	NA
.3	49.2	1.32	NA	NA
.5	48.9	1.32	0.2	60.3
.7	48.8	1.32	NA	NA

NA Not analyzed.

TABLE B-3. - $MgCl_2$-HCl-H_2O system

Solution			Wet residue		Solution			Wet residue		Solution			Wet residue	
HCl, pct	$MgCl_2$, pct	sp gr	HCl, pct	$MgCl_2$, pct	HCl, pct	$MgCl_2$, pct	sp gr	HCl, pct	$MgCl_2$, pct	HCl, pct	$MgCl_2$, pct	sp gr	HCl, pct	$MgCl_2$, pct
20° C					40° C					60° C				
0.0	35.2	1.33	NA	NA	0.0	36.0	1.35	NA	NA	0.0	37.6	1.39	NA	NA
3.0	32.0	1.32	1.2	40.9	2.3	34.0	1.34	1.1	39.8	1.4	36.2	1.38	0.5	42.2
6.4	28.7	1.30	NA	NA	5.2	31.2	1.33	2.3	38.8	3.4	34.5	1.37	1.0	41.5
8.5	26.6	1.29	3.6	37.5	6.1	30.3	1.32	1.9	40.6	6.1	32.0	1.35	1.7	41.8
11.1	24.1	1.28	NA	NA	9.0	27.4	1.31	2.9	39.7	7.4	30.9	1.34	.4	44.3
13.0	22.2	1.27	3.9	38.6	11.6	25.2	1.30	2.8	40.4	8.5	29.9	1.33	1.1	43.7
16.6	18.8	1.26	NA	NA	12.2	24.7	1.30	3.8	38.4	10.4	28.3	1.32	.8	44.4
18.3	17.2	1.25	3.9	39.5	14.6	22.6	1.29	3.9	38.8					
21.4	14.8	1.24	5.8	36.8	17.9	19.7	1.28	4.2	39.5					
22.5	13.8	1.24	NA	NA	21.4	17.1	1.27	4.3	39.3					
25.5	11.9	1.23	6.4	37.0	22.2	16.4	1.27	4.5	39.5					
26.0	11.1	1.23	NA	NA	23.6	15.3	1.26	4.0	39.8					
28.6	9.7	1.22	17.9	27.6										
30.4	7.0	1.22	NA	NA										
34.3	4.1	1.21	NA	NA										
36.3	3.0	1.21	17.4	28.9										

NA Not analyzed.

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TABLE B-4. - KCl-HCl-H_2O system (solution)

HCl, pct	KCl, pct	sp gr	HCl, pct	KCl, pct	sp gr	HCl, pct	KCl, pct	sp gr
	20° C			40° C			60° C	
0.0	25.5	1.17	0.0	28.4	1.18	0.0	31.0	1.20
2.8	20.8	1.15	2.9	23.9	1.17	2.5	26.8	1.18
6.0	15.9	1.13	5.9	19.2	1.16	5.2	23.0	1.16
9.6	11.0	1.12	9.1	14.3	1.14	8.2	18.5	1.15
12.8	7.1	1.11	12.2	10.7	1.13	10.9	14.9	1.14
16.7	4.8	1.11	16.3	6.7	1.12	14.1	11.1	1.13
21.5	2.5	1.12	20.0	4.3	1.12	16.9	8.6	1.12
23.8	2.0	1.13	24.4	2.7	1.13	19.5	6.7	1.11
25.7	1.7	1.13	27.6	2.2	1.14	21.8	5.3	1.12
27.8	1.3	1.14	30.8	1.7	1.15	24.1	4.3	1.13
29.7	1.1	1.15	32.4	1.6	1.16	26.5	3.5	1.13
31.5	1.1	1.16	33.8	1.6	1.17	30.4	2.6	1.14
33.7	1.1	1.17	35.0	1.5	1.18			
35.7	1.1	1.18	36.0	1.6	1.18			
38.2	1.2	1.19	36.5	1.7	1.19			
39.1	1.3	1.20						

TABLE B-5. - NaCl-HCl-H_2O system (solution)

HCl, pct	NaCl, pct	sp gr	HCl, pct	NaCl, pct	sp gr	HCl, pct	NaCl, pct	sp gr
	20° C			40° C			60° C	
0.0	26.1	1.20	0.0	26.6	1.20	0.0	27.0	1.20
4.9	18.9	1.17	2.1	22.7	1.19	2.7	23.1	1.18
10.0	11.7	1.14	4.5	19.8	1.17	6.1	18.6	1.16
14.5	6.5	1.12	7.2	16.2	1.15	9.1	14.6	1.15
19.1	2.8	1.12	9.7	13.0	1.14	11.8	11.2	1.13
23.5	.85	1.13	14.4	7.7	1.13	14.9	8.1	1.13
27.2	.35	1.14	17.8	4.9	1.12	17.7	5.8	1.12
35.7	.05	1.18	21.0	2.6	1.12	20.3	3.9	1.12
39.1	.05	1.19	23.5	1.5	1.13	22.7	2.6	1.12
			25.6	1.0	1.13	25.0	1.6	1.13
			27.7	.6	1.14	28.1	1.0	1.14
			29.2	.4	1.15	30.2	.8	1.15
			35.8	.2	1.18			
			37.0	.1	1.18			

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